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COLLABORATIVE RESEARCH AND DEVELOPMENT CONTRACT (CR&D)
Task Order 0072: Minority Leaders Nanocomposite Researcher

Merlin Theodore

Universal Technology Corporation

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Final Report

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MATERIALS AND MANUFACTURING DIRECTORATE
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14. ABSTRACT

This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted from 1 May 2007 through 1 May 2008. This research on nanocomposites in support of the Minority Leaders Nanaocomposite Program currently in progress at AFRL/RXBC. This research encompassed processing nanomaterials with various functional groups onto composites and measuring improvements in mechanical, electrical, and thermal properties. Characterization in the nanoscale was performed using AFM, SEM, and TEM. Although it is well-acknowledged that carbon fibers possess excellent thermal conductivity (TC), direct measurement of thermal conductivity of individual carbon fibers under steady-state heat flow conditions is very difficult, and only limited studies have reported such TC values. These TC values have been correlated with electrical conductivity (EC) values, and often these TC-EC correlations are used in conjunction with EC measurements to indirectly estimate TC values. Unsteady-state heat transport phenomenon has also been utilized to obtain thermal diffusivity values, from which TC values can be calculated. The laser-flash technique was proposed a number of years ago, and has developed into a standard technique for homogeneous bulk materials. It is efficient and offers rapid measurement times (from milliseconds to a few seconds). It requires only small sample dimensions, and analysis of multi-layer samples is possible. Here we report on longitudinal TC measurements on various pitch- and PAN-based carbon fibers from laser-flash measurements on their composites. Because carbon-fiber composites are highly anisotropic and non-homogeneous, various limitations of the experimental technique and accompanying analysis are discussed, and suggestions for improvements are made.

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Thermal Conductivity Measurements for Carbon Fibers

1.0   INTRODUCTION

Although it is well-acknowledged that carbon fibers possess excellent thermal conductivity (TC), direct measurement of thermal conductivity of individual carbon fibers under steady-state heat flow conditions is very difficult, and only limited studies have reported such TC values. These TC values have been correlated with electrical conductivity (EC) values, and often these TC-EC correlations are used in conjunction with EC measurements to indirectly estimate TC values. Unsteady-state heat transport phenomenon has also been utilized to obtain thermal diffusivity values, from which TC values can be calculated. The laser-flash technique was proposed a number of years ago, and has developed into a standard technique for homogeneous bulk materials. It is efficient and offers rapid measurement times (from milliseconds to a few seconds). It requires only small sample dimensions, and analysis of multi-layer samples is possible. Here we report on longitudinal TC measurements on various pitch- and PAN-based carbon fibers from laser-flash measurements on their composites. Because carbon-fiber composites are highly anisotropic and non-homogeneous, various limitations of the experimental technique and accompanying analysis are discussed, and suggestions for improvements are made.

2.0   EXPERIMENTAL

Carbon fiber tows were consolidated into thin layers using a low-viscosity cyanoacrylate or a polyester resin, and then embedded into the polyester casting resin. The solidified composite rods were sectioned into disks ($\approx$1 to 3 mm thick) and their thermal conductivity was measured using two different thermal flash units (Neztsch LFA 447 and 427). The lower surface of a plane-parallel sample is heated by a short laser pulse. The temperature rise on the top surface is measured as a function of time using an IR-detector. It is noted that if the samples were partially transparent, significant error resulted from laser light penetration into the sample. Therefore, samples were coated with gold or silver (about 100 nm coating thickness) and then a thin layer of graphite powder was sprayed on both sides of the sample following ASTM E1461.

Thermal diffusivity of a material (α) can then be calculated from unsteady-state thermal transport equations and the measured half-time ($t_{\frac{1}{2}}$) for the sample temperature to rise by half of the maximum ΔT. Thermal conductivity is then expressed as:

$$k = \alpha * \rho * C_p \text{ [W/(m*K)]}$$

where k is the thermal conductivity (W/m-K), Cp is specific heat capacity (J/g-K), ρ is the density (g/cm^3), and α represents the thermal diffusivity (mm^2/s) of the composite material. The experimentally obtained values of thermal diffusivity are for the composite (α_c), and must be converted into fiber diffusivity values using rules of mixture. For carbon fibers, specific heat capacity $C_f = 0.73$ J/g.K and density $\rho_f = 2.1$ g/cm^3. For the solidified resin matrix, $C_m = 1.3$ J/g.K

and density $\rho_m = 1.2$ g/cm^3. Then, the products $C_f * \rho_f = 1.53$ J/K. cm^3 and $C_m * \rho_m = 1.56$ J/K. cm^3, i.e., the product of density and heat capacity for fibers and matrix are approximately equal. Consequently,

$$\rho_c C_c = C_m \rho_m = C_f \rho_f \text{ and } \alpha_c = v_f \alpha_f + v_m \alpha_m$$

However, $\alpha_m \approx 0.1$ mm^2/s and $v_m \approx 0.8$. So, for values of α_f greater than about 4 mm^2/s, the matrix contribution to diffusivity is less than 10% and may be ignored. Thus,

$$\alpha_f \approx \alpha_c / v_f$$

3.0   RESULTS

Typical intensity curves for P25 pitch-based carbon fibers are shown in Fig.1 with model fits assuming adiabatic conditions ("Parker") and heat loss conditions ("Cowen"). From the above composite analysis, the thermal diffusivity for fibers were determined to be 9.1 and 9.3 mm^2/s, respectively, for adiabatic and heat-loss models; the calculated fiber conductivity values for the sample were 14.0 W/m.K and 14.3 W/m.K, not very different. The average axial thermal conductivity for P25 pitch-based carbon fibers, based on two replicates, was 13.1 W/m.K, as compared with a reported value of 22 W/m.K. For P100 carbon fibers, the conductivity values for two replicates were measured to be 508 and 530 W/m.K, whereas the reported value is 520 W/m.K. For PAN-based T300 carbon fibers, conductivity was measured to be 10±1 W/m*K, quite consistent with literature values of 10 W/m*K. We emphasize that the quality of the results are highly sensitive to the uniformity of sample dimensions, particularly sample thickness. Thickness variations of 0.013 mm within the P100 samples can result in variation of ± 60 W/m.K. Ongoing work focuses on further verification of the calculated values using finite element analysis to account for the non-homogeneous material. Additional measurements are being conducted on various commercial and experimental nanocomposite carbon fibers, such as K-13C, K-139, AS-4, and M-60.
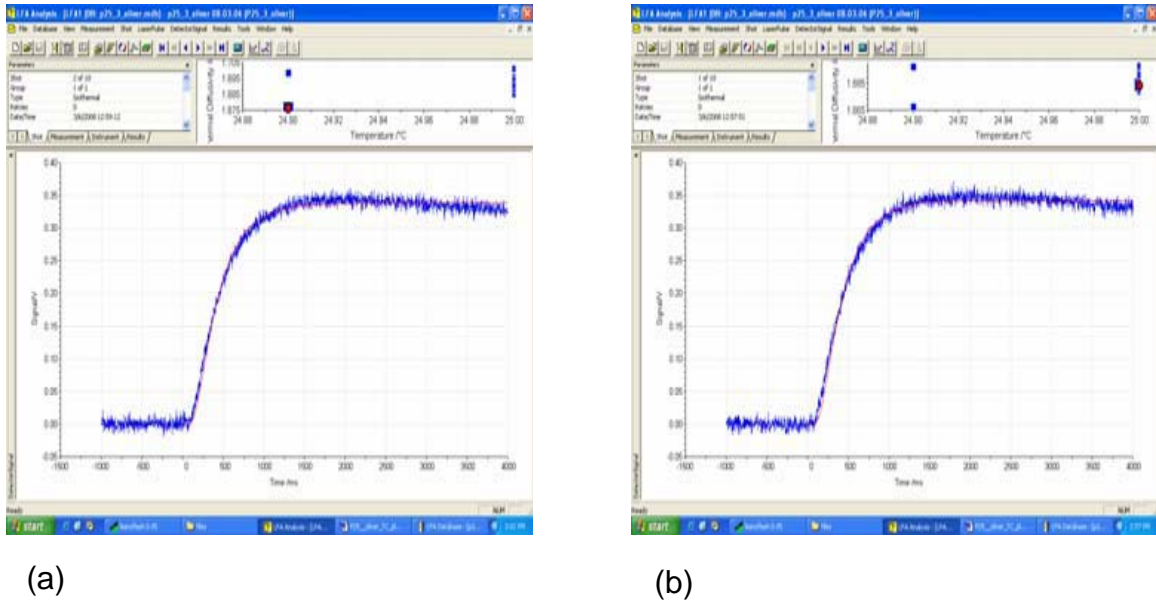

(a)   (b)

Figure 1. Response of IR-detector after laser-flash. Data fitted with (a) adiabatic model, and (b) heat-loss model.

6.0 NANOSTRUCTURED COUPLING AGENTS FOR MULTIFUNCTIONAL COMPOSITES

Nanoengineered composite materials, in which one or more of the composite constituents (eg., matrix, fibers, laminates) is nanostructured and possesses enhanced and functional properties, represent a potentially enabling technology for a wide range of DoD and civilian applications. For example; future aerospace and electronic systems will demand materials with elements of integrated "functionality" such as thermal management, in addition to excellent mechanical and electrical properties, dimensional stability, low outgassing, and electromagnetic shielding. However, there are significant challenges related to the synthesis and processing of these "multiscale" composites that must be addressed in order to exploit the true potential that nanotechnology holds for composites.

The interface plays a significant role in the behavior of traditional and nanoscale composites. This is the region in the vicinity of the particle in which the polymer properties are altered as compared to the bulk. Traditional composites have a significant body of knowledge on how to control the fiber-resin interface by changing the chemistry of the filler surfaces. Understanding of nanocomposite interfaces is even more critical than that of traditional composites because it represents a much larger volume fraction. Furthermore, the number of interfaces increases in a multiscale composite, further complicating the issue.

We have recently developed nanostructured coupling agents designed to couple micron scale reinforcements to the composite matrix. We will report on the synthesis of these structures their incorporation into fiber reinforced laminates and the resulting properties.

We have successfully created covalent bonds between amine modified carbon nanotubes ($CNT-NH_2$) and epoxy modified carbon fibers (CF_E) using the electrophoresis method. Preliminary covalent bonding studies also include the spray method. Several batches were prepared; spray method using a big and small nozzle, electrophoresis method using 0.001% and 0.005% of $CNT-NH_2$ in DMF solution. All batches were tested on Raman, TGA-mass Spectroscopy, SEM, and XPS to determine the interfacial properties. The electrophoresis method was also used for alignment of $CNT-NH_2$ in the longitudinal direction onto the surface of the CF_E with the aid of a magnetic field.

4.1 Minority Leaders Responsibilities

The goal for this quarter was to complete and coordinate the summer program. We have selected 15 students from the mentor universities, Historically Black College and Universities (HBCU), and Dayton Early College Academy (DECA). All students are paired up with an AFRL summer advisor. These summer advisor are employed in the Materials and Manufacturing (Hybrids, Polymer and Thermal branch), and Human Effectiveness directorates. The summer program is ten weeks long and a detailed calendar of events was developed to keep the students occupied for the full ten weeks. Students are scheduled to report their research results every Friday. We also scheduled life skills, presentation skills, resume writing, and leadership skills workshops to enhance the student capabilities.